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Direct Reaction of Silicon with Ethyl Chloride in a Fluidized Bed Reactor

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Direct Reaction of Silicon with Ethyl Chloride in a Fluidized Bed Reactor

Ihsan Hamawand, Thamer Mohammed, and Moayyed G. Jalhoom

Abstract

The aim of this work was to study the production of diethyldichlorosilane $[(C_2H_5)_2SiCl_2]$. The catalytic reaction of silicon (Si) of purity 99.9% with ethylchloride (C_2H_5Cl) was investigated in a fluidized bed reactor. Cuprous chloride ($CuCl$) of purity 99.9% was used as a catalyst of the reaction. Gas chromatography was used on-line for analysis of the reaction products. The experimental work was carried out using a stainless steel column of 5cm internal diameter and 50cm height as the fluidized bed reactor.

The experiments start with different bed temperatures between 200 and 300 C to identify the optimum reaction temperature. This temperature was found to be at 250 C, which resulted in the maximum of ethylchloride ($EtCl$) conversion and diethyldichlorosilane yield. In fifteen runs, the variables considered were sieve-analysis average particle size d_p (50,100, and 150 μm), contact mass weight wt (100 – 200 gm) and reacted gas velocity U_g (1.41 – 2.83 cm/s). It was found that the conversion of $EtCl$ increases with decreasing reacted gas velocity, increasing bed contact mass and particle diameter. The yield of Et_2SiCl_2 was not affected by these variables, but bed temperature was found to have a significant affect.

Two mathematical models, the Orcut model and the continuous CSTR model were used to predict theoretical data for the conversion of $EtCl$. The comparison between the experimental and the theoretical data showed good agreement with an absolute error of less than 9%.

KEYWORDS: organohalosilane, direct process, organosilicon, ethylchlorosilane, diethyldichlorosilane

Introduction

The discovery of the 'Direct Synthesis' or 'Direct Process' for organochlorosilanes by Rochow and Muller, generally referred to as the Rochow process, promptly led to the first practical large scale production of organosilanes and silicone polymers. The silicones industry proceeded to expand rapidly starting in the 1940's.

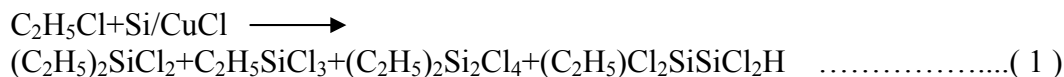
Rochow (1945), effected a reaction between the silicon and the hydrocarbon halide while the latter was in vapor state, and, associated with a metallic catalyst (e.g. copper) for the reaction.

Rochow and Patnode, (1945), found that the efficient utilization of methyl chloride is enhanced as the proportion of the metallic catalyst, specifically copper, is increased up to about 10. Ward and et al., (2001), described a method for enhancing the formation of alkylhalosilane during the direct method reaction between powdered silicon and a catalyst comprising copper, zinc, tin, and phosphorus.

The direct process is operated primarily for the commercial production of methylchlorosilanes for this reason the most published papers and patent are concerned the reaction of silicon and methylchloride [Bablin et al.(2002), De Cookerand et al., 1975, Flaquent et al., 1994, Gasper Galvin et al., 1991, Jung, 1996, lewis Larry N. et al., 20002]. Ethylchlorosilanes were manufactured in the soviet union, polyethylsiloxane products used in various branch of engineering; fluids, lacquers, rubbers, elastomers, compounds [Endovin 1997]. Ethyl silicones produced from $(C_2H_5)_2SiCl_2$ like methyl and phenyl polymers, are used in electrical varnishes, hydraulic and heat transfer fluids and lubrication however $(C_2H_5)SiHCl_2$ is the major objective of commercial operation in the Soviet Union, the objective is unknown [Lewis and Rethwish, 1993].

A great number of papers have been written about how to increase the selectivity for dimethyldichlorosilane which result from the reaction of silicon with methylchloride and copper (or its compounds as a catalyst), promoters [Kuivila et.al., 1996, Kim et.al., 1992, Olakangil et.al., 2000], however there is little known about the reaction with ethylchloride. Ethylchloride was chosen to be the reacted gas with silicon as the topic of this paper given the lack of published literature.

The copper catalyzed reactions of ethyl halides with silicon give fair yields of the corresponding ethylhalosilanes. Some of the many reaction products are shown in Equations (1).



The uncatalyzed reaction of ethyl chloride with silicon is initiated above 300°C . This event may be the result of dehydrohalogenation of ethyl chloride and subsequent reaction of ethyl chloride with trichlorosilane. In the presence of copper, initiation occurs about 200°C . Selectively to $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ is improved by copper catalysis and lower reaction temperatures. Under favorable catalytic and fluidization conditions, $(\text{C}_2\text{H}_5)_2\text{SiCl}_2$ yields of up to 65wt. % are obtained [Lewis and Rethwish, 1993].

The aim of the present work was to investigate the Production of product mixture especially Et_2SiCl_2 by the reaction of EtCl with silicon using CuCl as catalyst in fluidized bed reactor at different parameters: temperature of the bed, particle diameter, contact mass and reacted gas velocity (EtCl), to find the optimum values and the interaction between these variables. Et_2SiCl_2 is selected as the desired product due to its application in the production of polymers. The advantage compared to Me_2SiCl_2 it can significantly cheapen the manufacture of organohalosilanes polymers as the boiling points of the ethylchlorosilanes are more widely spread from each other and the separation requires fewer column.

Experimental Work

A stainless steel column with (5cm) inner diameter and (50cm) height was used as the ethylchlorosilane reactor, an electrical heater rod with (1.5m) was turned around the column, the outlet from the reactor was connected to a cyclone to collect the fine particle to be recycled to bed; off-gas from cyclone go to a filter to collect any particle that cyclone did not catch. Solids-free off-gas from the filter entered the condenser or the GC. The condenser used ethanol as a cooling liquid, a chiller was used to cool the ethanol and a pump used to recycle the liquid through the condenser. Figure (1) show parts of the reactor system.

The silicon crystal grinder was designed and assembled for this purpose combined of a pressure vessel with stainless steel blades connected to high speed motor at the bottom of the vessel. The silicon crystals were crashed first with a hammer to suitable size for the grinder and then grinded with different residence time in the grinder to have different particle size.

The particle size distribution (PSD) was simply done by using different mesh sizes of sieves. Four sieves were used in series; at the top 175 micrometer followed by 125, 75, and 25 micrometer sieves. Silicon particles that trapped in between these trays are collected separately. The average silicon particle size was estimated from the maximum and the minimum sizes of every two parallel meshes. Table (1) lists the average silicon particle size between every two meshes;

Particle size in micrometers		
Min.	Max	average
25	75	50
75	125	100
125	175	150

Table (1): The average silicon particle size between every two meshes.

Two temperature readers were used, one connected to selector to read temperature in three places (gas inlet, inside the reactor, and the outlet gas), the second read and control the temperature inside the bed.

Analysis:

Gas chromatography was used to analyze the reacted gas and the product on-line directly. The GC name is 'Gaw-Mac Spectra' by Gaw-Mac internment Co. LTD. The retention times for each product are shown in table (2). Table (2) shows the major product of the reaction, other products with less than 1 % were neglected.

Product	RT <i>min</i>	Boiling points <i>°C</i>
EtCl	1.02-1.12	12.2
Et(H)SiCl ₂	2.78-2.9	75
EtSiCl ₃	4.06-4.74	100
Et ₂ SiCl ₂	8.95-9.2	130
Et ₃ SiCl	9.72-9.69	144

Table (2): The retention time for the product mixtures.

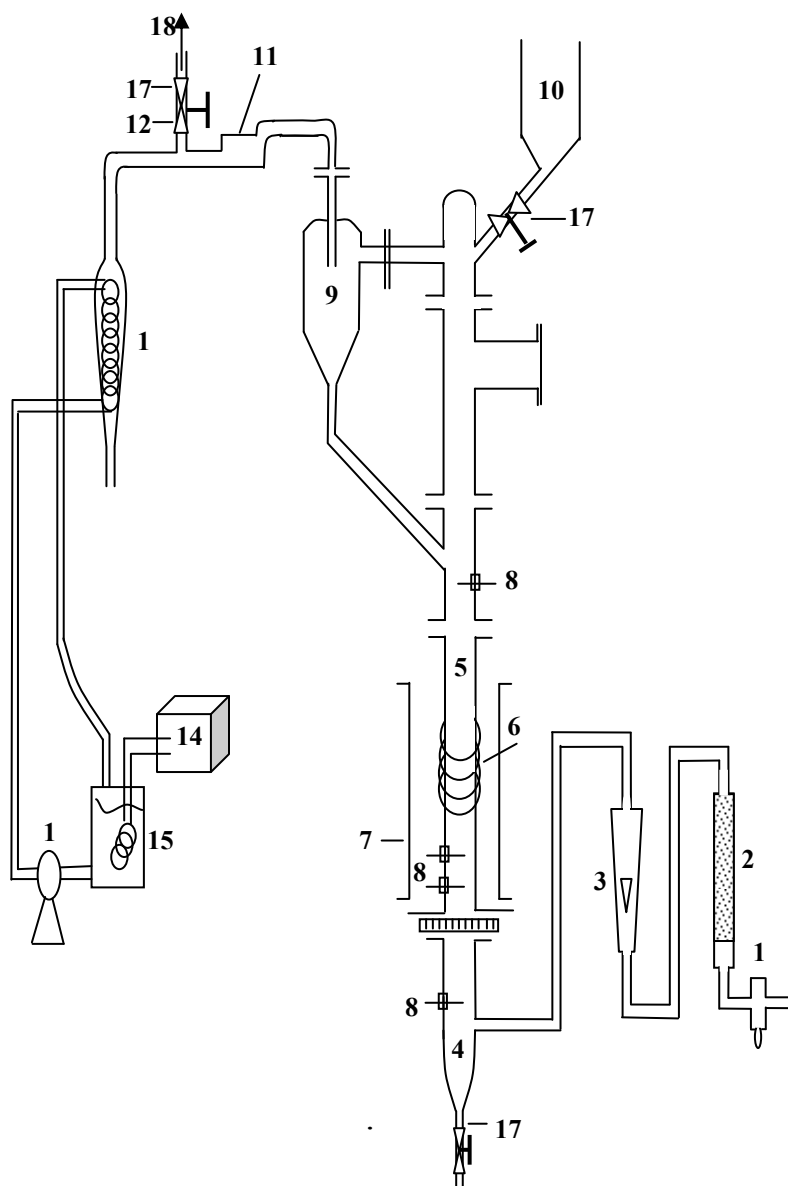


Figure (1); Reactor system, 1- air filter , 2- silica gel column, 3- flow meter, 4- stainless steel cone under distributor, 5- stainless steel column (diameter = 5 cm), 6- electric heater, 7- jacket aluminum covered with fiber glass, 8- sensors, 9- cyclone, 10- stainless steel feed storage, 11-product filter , 12- connection to GC, 13- condenser, 14- Chiller, 15- ethanol storage vessel, 16- pump, 17- valve, 18- line goes to GC

Material specification

Silicon [Si];

Reference; Ibn Sina State Company / Baghdad – Iraq.

Name: Silicon

Description: crystalline, reflective bluish-black

Molecular formula: Si

Molecular Weight: 28

Density: 2.3290 g/cm³

Boiling Point: 1414 C

Melting Point: 3265 C

PROPERTY (SOLID PHASE)	SPECIFICATION
Si, Wt. %	99
Fe	2000 ppm
Al	2000 ppm
Zn	250 ppm
Ca	200 ppm
P	20 ppm

Cuprous Chloride [CuCl];

Reference; Aldrich

Name: Cuprous Chloride

Description: Greenish Yellow Powder

Molecular formula: CuCl

Molecular Weight: 99

Density: 3.53 g/cm³

Boiling Point: 1490 °C C

Melting Point: 430 C

PROPERTY (POWDER)	SPECIFICATION
CuCl, Wt. %	99.995+ % trace metals basis
Moisture	less than 0.5%
Insoluble	less than 100ppm
Water Soluble	less than 5%
Iron Content	Max 30 ppm
Total Copper	Min 62.5%

Ethylchloride [EtCl];

Reference; Ibn Sina State Company / Baghdad – Iraq.

Name: Ethyl Chloride

Description: Colorless Gas

Molecular formula: C₂H₅Cl

Molecular Weight: 64.52

Density: 0.9214 g/cm³

Boiling Point: 12.3 C

Melting Point: -138.7 C

PROPERTY (GAS PHASE) SPECIFICATION

Ethyl Chloride, Wt. %	99
HCl,	<10 ppm
Nonvolatile Matter,	<10 ppm
Water,	<150 ppm

Experimental Procedure

A Typical run began with preparing an amount of pulverized silicon with loading of 15 weight % CuCl [catalyst] of the silicon contact mass, [Wessel and Rethwisch, 1996, Lewis and Ward, 2002], and pouring it inside the reactor from the top. 15 weight % of CuCl was selected for the entire of the experiments due to its higher production of diethyldichlorosilane compare to the other products. The Cu counts of around 10 % of the contact mass because the CuCl contain 62.3 % Cu. The comparison with other percentages CuCl was left over for further work.

Promoter's usage in methylchlorosilane is to increase the selectivity for diethyldichlorosilane product. The silicon itself contains some impurities including one of the promoters such as Zinc. The promoters have not been used in this study as the CuCl catalyst and the silicon composition used gave the highest diethyldichlorosilane. Usage of promoters could be potential for further work. Set the controller on the reaction temperature (250°C), [Lewin, 2001, Aramata et.al., 2002], the heater began to work slowly because it was connected to voltage variant which was set on 60%. The temperature rise slowly, to avoid any deflection so the temperature of the reactor did not rise more than ±5°C after reaching the set point of 250°C. Nitrogen (inert gas) was supplied to the reactor at low flow rate after it flowed through 2m long pipe inside furnace to preheat the gas to (150-200°C), then after 15min the flow of Nitrogen was stopped and flow of Ethylchloride (EtCl) began to enter to the pre-heater and then to the reactor.

The tube that carried the product was divided into two lines, one going to the condenser and the other to the GC. When we wanted to analyze the product,

the line going to the condenser was closed and the line to the GC was opened and vice versa.

Every 20 *min* the product was injected into the online GC for analysis. These steps were repeated for each parameter.

Models Applied to the Reaction

Two models were used to show the behaviour of the reaction. The first model, which uses the design equation of CSTR, shows the conversion of EtCl as a function of temperature of reaction, contact mass of the bed, molar flow rate of reacted gas, and time, [Voorhoeve, 1997].

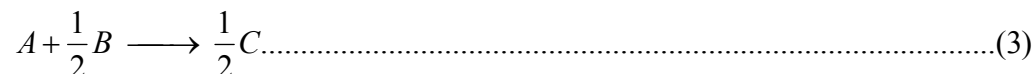
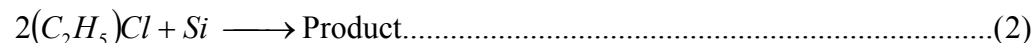
In the second model, a material balance was done on the bubble phase to predict the conversion of EtCl as a function of variables included in the design of fluidized bed reactor such as; diameter and height of the bed, temperature of reaction, fluidizing velocity, particle diameter, contact mass (weight of the bed), [Kunni, 1969, Levenspiel, 1999, Geldart, 1986].

Model (1) Kinetic Model

Using the design equation for CSTR reactor (well mixed) which is very near in behavior to fluidized bed reactor [Fogler, 1997].

Also assumed first order decay equation for the deactivation of CuCl catalyst, the deactivation may be a result of formation of coke over the surface of the catalyst [Wessel and Rethwisch, 1996], and also for the decrease in silicon concentration because of consumption.

The final equation after these assumptions shows the conversion of EtCl. The theoretical data from this equation compared with the experimental one and it shows a good agreement.



$$\theta_B = 0 \dots\dots\dots (4)$$

The design equation of CSTR is;

$$-r'_A = \frac{F_{Ao} \cdot X_A}{wt} = \frac{gmol}{gm \cdot S} \dots\dots\dots (5)$$

$$F_{Ao} = v_o C_{Ao} = U \cdot A \cdot \frac{Pt \cdot Y_{Ao}}{R_g \cdot T_o} \dots\dots\dots(6)$$

$$-r'_A = K_n \cdot C_A^n \cdot a \dots\dots\dots(7)$$

Assuming first order deactivation, gives;

$$-\frac{da}{dt} = K_d \cdot a \dots\dots\dots(8)$$

$$-\frac{da}{a} = K_d \cdot dt \dots\dots\dots(9)$$

$$a = e^{-K_d \cdot t} \dots\dots\dots(10)$$

$$C_A = C_{Ao} \frac{(1 - X_A)}{(1 - 0.667X_A)} \cdot \frac{T_o}{T} = \frac{PY_{Ao}}{R_g \cdot T_o} \cdot \frac{(1 - X_A)}{(1 - 0.667X_A)} \cdot \frac{T_o}{T} \dots\dots\dots(11)$$

Assume first order reaction ($n=1.0$), [Rethwisch and Wessel 1996 , Bablin et.al. 2002]

$$\frac{F_{Ao} \cdot X_A}{wt} = K_1 C_{Ao} \frac{T_o}{T} \cdot \frac{(1 - X_A)}{(1 - 0.667X_A)} \cdot e^{-K_d \cdot t} \dots\dots\dots(12)$$

$$e^{+K_d \cdot t} = \frac{K_1 \cdot wt \cdot T_o}{v_o \cdot T} \cdot \frac{(1 - X_A)}{X_A (1 - 0.667X_A)} \dots\dots\dots(13)$$

$$\ln \frac{(1 - X_A)}{X_A (1 - 0.667X_A)} = \ln \frac{v_o \cdot T}{K_1 \cdot wt \cdot T_o} + K_d \cdot t \dots\dots\dots(14)$$

$\xleftarrow{\text{intercept}} \quad \xrightarrow{\text{slop}}$

A statistical program was used with experimental data from Table (3) to predict intercept and slope.

t (sec.)	$T = 200^{\circ}C$		$T = 250^{\circ}C$		$T = 300^{\circ}C$	
	X_A	$\ln \frac{(1-X_A)}{X_A(1-0.667X_A)}$	X_A	$\ln \frac{(1-X_A)}{X_A(1-0.667X_A)}$	X_A	$\ln \frac{(1-X_A)}{X_A(1-0.667X_A)}$
1200	0.03	3.4963	0.129	1.9998	0.148	1.854
2400	0.047	3.0413	0.157	1.7913	0.17	1.705
3600	0.06	2.7923	0.149	1.8471	0.15	1.840
4800	0.053	2.9189	0.143	1.8908	0.13	1.991
6000	0.045	3.0855	0.137	1.9362	0.11	2.166
7200	0.018	4.01129	0.128	2.008	0.088	2.398

Table (3): Conversion of EtCl at different temperature (Experimental).

Set Eq.(16) as a linear equation as below

$$V_2 = a + b \cdot V_1 \dots \dots \dots (15)$$

Where $V_2 = f(X_A)$, $V_1 = t$, and a, b are constant.

The constants of Eq.(17) are predicted by statistical program as shown in Table (4).

T	a	b	R
200	1.4807	0.000319	0.893
250	1.6852	0.00004358	0.995
300	1.3352	0.000143	0.994

Table (4): The value of constant (a, b) in Eq.(17).

Input variables:

$$wt = 150gm, \quad v_o = A \cdot U = 27.685 \text{ cm}^3 / s$$

$$v_{o250} = 27.685 \cdot \frac{250 + 273}{30 + 273} = 47.786 \text{ cm}^3 / s$$

$$a = \ln \frac{v_o \cdot T}{K_1 \cdot w \cdot T_o} \dots \dots \dots (16)$$

Substituting the value given above in Eq.(18); then the rate of reaction is;

$$K_1 = \frac{v_o \cdot T}{w \cdot T_o} \cdot e^{-a} = 8.541 \times 10^{-4} T e^{-a} \dots\dots\dots(17)$$

Substituting the values of (a) in Eq.(19) we can have the rate of reaction at different temperature as shown in Table (5).

T	a	K_1
200	1.4807	0.091898
250	1.685	0.08283
300	1.3352	0.12876

Table (5): Rate of reaction for different temperature.

Using the data for (K_1) in Table (5), to predict the constant in Arrhenius equation.

$$K_1 = A \cdot e^{-E/R_g \cdot T} \dots\dots\dots(18)$$

$$K_1 = 13.95977 e^{\frac{-220314.57}{R_g \cdot T}} \quad R = 0.9998 \dots\dots\dots(19)$$

Eq.(21) represent the rate constant

We predict the deactivation rate constant from the slop of Eq.(17) as shown in Table (6)

T	$b = K_d$
200	0.000319
250	0.000044
300	0.000143

Table (6): Deactivation rate versus temperature.

Assuming polynomial equation to fit the data in Table (6).

$$K_d = a + b \cdot T + c \cdot T^2 \dots\dots\dots(20)$$

$$K_d = 5.159 \times 10^{-3} - 3.916 \times 10^{-5} \cdot T + 7.48 \times 10^{-8} \cdot T^2 \quad R = 1.00 \dots\dots\dots(21)$$

Eq.(22) represent the deactivation rate constant.

The reaction rate equation is:

$$-r'_A = K_1 \cdot C_A \cdot e^{-K_d t} \dots\dots\dots(22)$$

Back to CSTR design equation;

$$\frac{F_{Ao} \cdot X_A}{wt} = 13.95977 e^{\frac{-220314.57}{R_g \cdot T}} \cdot \frac{P_t \cdot Y_{Ao}}{R_g \cdot T} \cdot \frac{(1 - X_A)}{(1 - 0.667 X_A)} \cdot e^{-K_d t} \dots\dots\dots(23)$$

The conversion of EtCl then is:

$$X_A = \left(\frac{wt}{F_{Ao}} \right) \cdot 13.957 \cdot \exp \left[\frac{-220314.57}{R_g \cdot T} \right] \cdot \frac{P_t \cdot Y_{Ao}}{R_g \cdot T} \cdot \frac{(1 - X_A)}{(1 - 0.667 X_A)} \cdot e^{-K_d t} \dots\dots\dots(24)$$

Where K_d is represent by Eq.(23), X_A is the amount of ethylchloride converted to product which represent the percent of ethylchloride enter to the reactor (100%) minus percent recorded at the outlet.

Eq.(26) was used in a computer program to predict theoretical result for conversion of EtCl, the equation go through a trial and error method.

Fluidized Bed Model (2) Orcut Model

Assuming no particles in the bubble phase, the change in molar flux of species A at any height in the bubble phase must be accounted for by interphase transfer [Eurgen, 1999]

$$X_A = \frac{K'_1(1 - \beta e^{-x})}{1 - \beta e^{-x} + K'_1} \dots\dots\dots(25)$$

Eq.(27) was used in a computer program to predict theoretical result for conversion of EtCl.

Where:

$$K'_1 = K_1 e^{-K_d t} \frac{H_{mf}(1 - \epsilon_{mf})}{U} \dots\dots\dots(26)$$

$$x = \frac{K_q a_b \epsilon_b H}{\beta U} \dots\dots\dots(27)$$

$$\beta = \frac{U - U_{mf}}{U} \dots\dots\dots(28)$$

Results and Discussions

The experiments included the study of the catalytic reaction for different variables: Velocity of reacted gas, particle diameter, and weight of the contact mass. Conversion of EtCl and percent of Et_2SiCl_2 measured with time were experimental results which were compared with the models.

Conversion of reacted gas EtCl with time at different temperatures is shown in Figure (2). The conversion of EtCl for each temperature increases in the first half hour then start to decline. The increase in conversion of EtCl may be due to increase in formation the (η - phase; Cu_3Si) with time which is reported by [Weber et.al., 1989; Ward et.al., 2000; Lewis and Ward, 2002; Weber et. al., 1989; Ward et. al., 2000]. These references are concerned with eta phase in production of methylchlorosilanes. Eta phase is not measured for the work reported in this paper but assumed to follow the analogous methylchlorosilane chemistry. This is could be subject for further work as the eta phase has been reported as key factor in the production. The decline is decay in the catalyst which may due to the formation of coke which is responsible for the decrease in conversion as reported by [Wessel and Rethwisch, 1996]. Cracking products have not been considered in this paper and only assumed theoretically that coke formation is the only parameter that results in decline in the conversion of EtCl.

Also Fig.(2) shows the increase in conversion of EtCl as the temperature of the reaction increases from 200C to 300 C. The average optimum conversion of EtCl is at 250 C, also this temperature has been reported as the best and stable temperature for the reaction [Lewin, 2001, Aramata et. al., 2002].

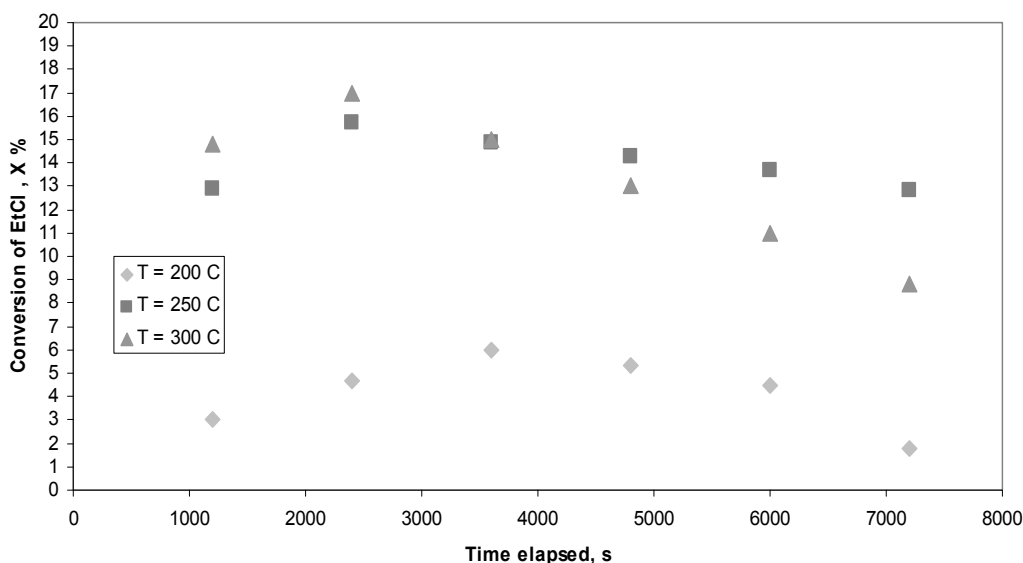


Figure (2); Conversion of ethyl chloride at different temperature

Figure (3) shows the percent of Et_2SiCl_2 in the product at different reaction temperature. The individual component conversion represents the percent of individual components in the product excluding the unreacted ethylchloride. It is clear from the figure that 250 C is preferable for optimization of Et_2SiCl_2 production compared to 200 C and 300 C. This lead to select the temperature of 250 C for the reminder of the experiments as it shows the optimum percentage of conversion and desired product yield.

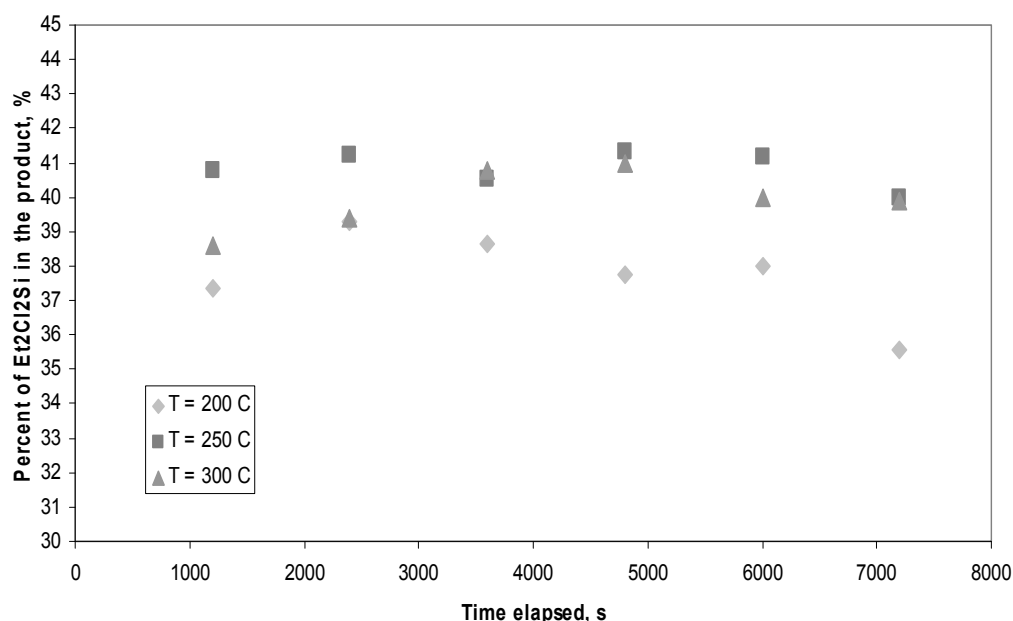


Figure (3); Percent of diethyldichlorosilane in the product at different temperature

Three figures (4), (5), and (6) have been plotted to show the effect of the reacted gas velocity, weight of the contact mass and the silicon particle diameter. As expected the decrease in the reacted gas velocity resulted in higher conversion of EtCl as shown in Figure (4). Lower velocity of the inlet gas results higher the residence time of the reacted gas. Double the weight of the contact mass (silicon and catalyst) led to 100 % increase in the conversion of the EtCl , which is due to increase in the contact time between the reacted solid and the gas, figure (5).

Despite the small increase in the conversion due to increase in the silicon particle diameter, the particle diameter effect can be neglected as the deviation in the conversion for the three selected diameters are between 1 to 2 %, figure (6). The conversion changes are not statistically significant.

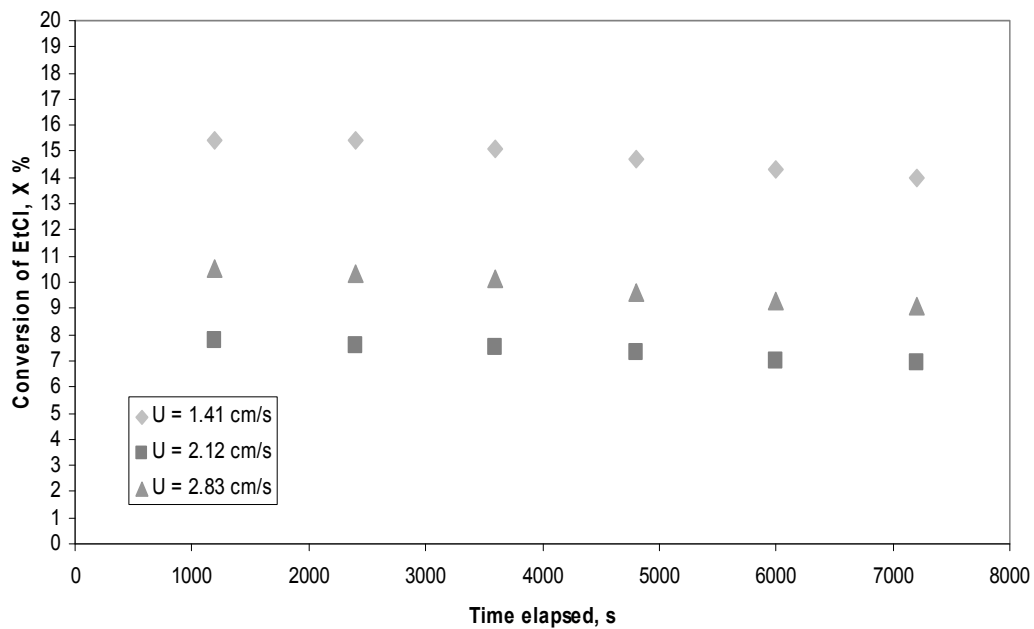


Figure (4); Conversion of ethyl chloride at different reactant gas inlet velocity

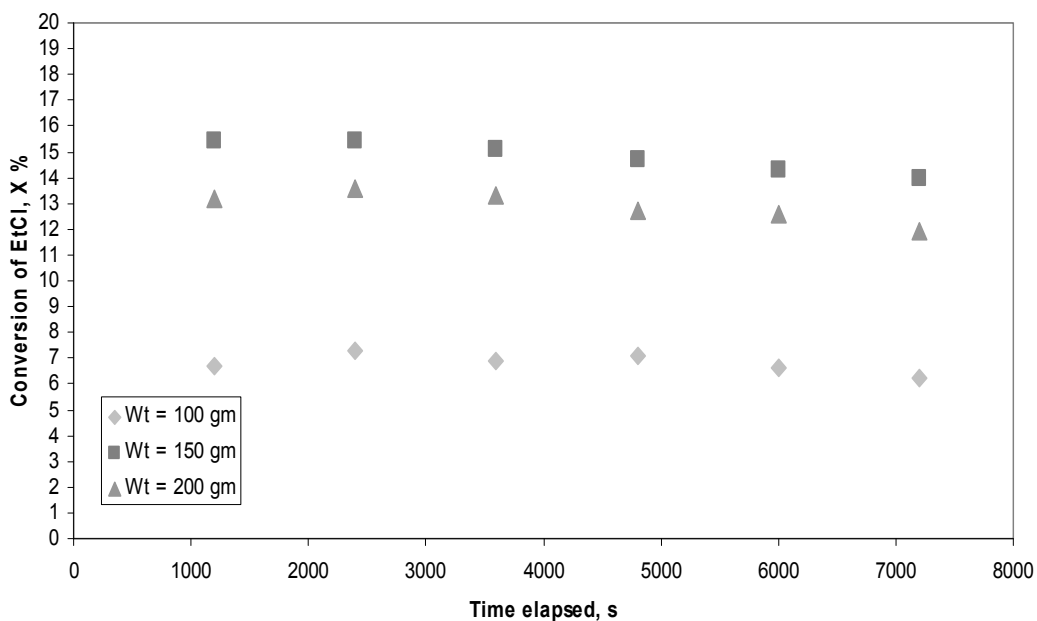


Figure (5); Conversion of ethyl chloride at different weight of solid in the bed

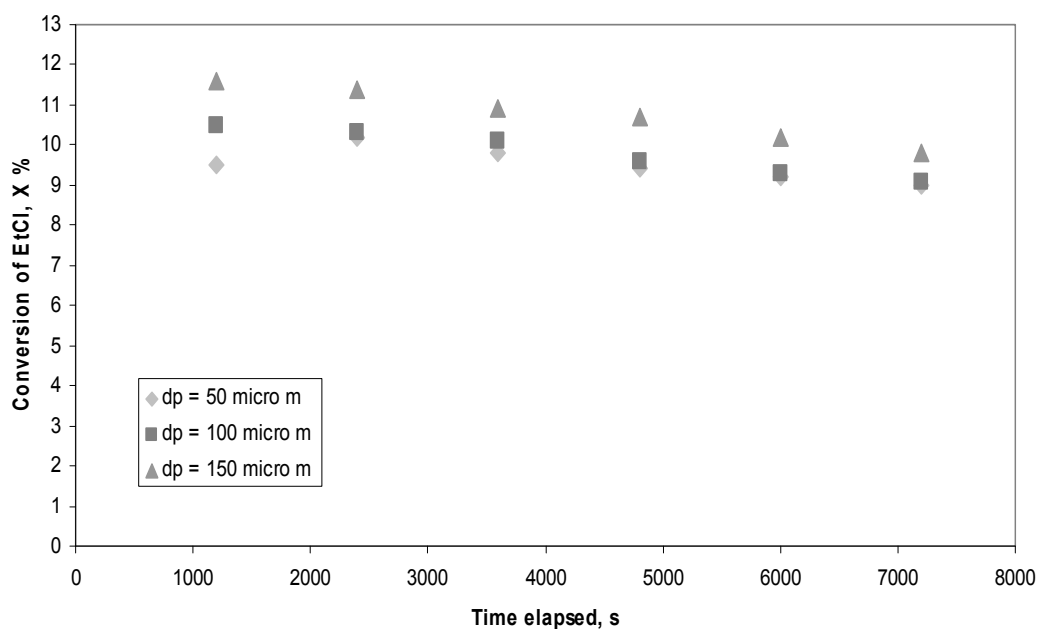


Figure (6); Conversion of ethyl chloride at different silicon particle diameter

Figures (7) to (11), show the comparison between the experimental and the calculated data from the models: model-1 kinetic model, and the model-2 the fluidized bed model. The standard absolute error lies between (2-9) % for different particle diameters, weights of the contact mass, and velocity of reacted gas.

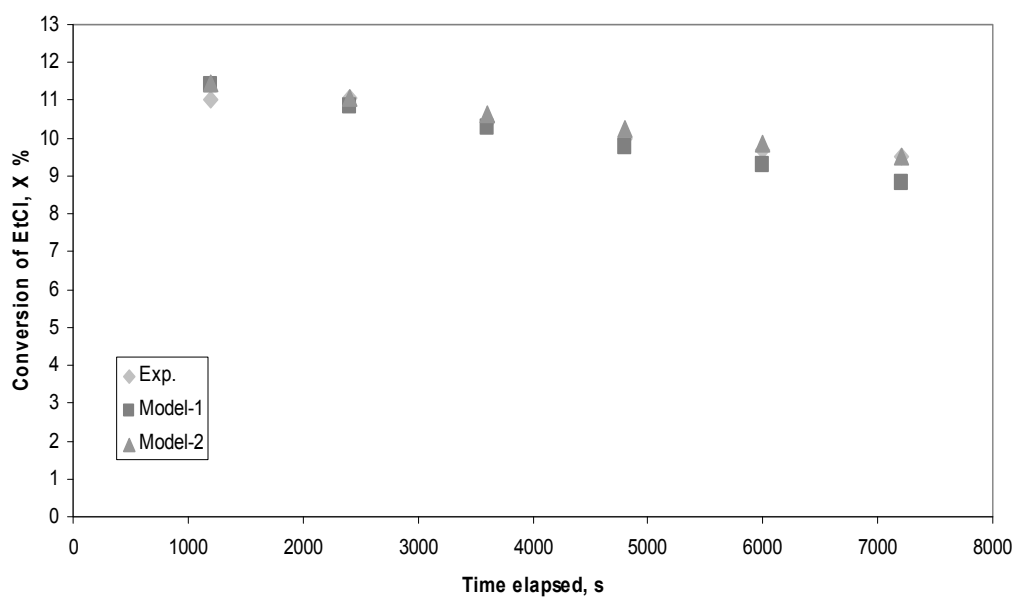


Figure (7); Comparison of the experimental ethyl chloride conversion with the two models, $W_t = 120$ gm, $U = 1.6$ cm/s, $d_p = 75$ micrometer

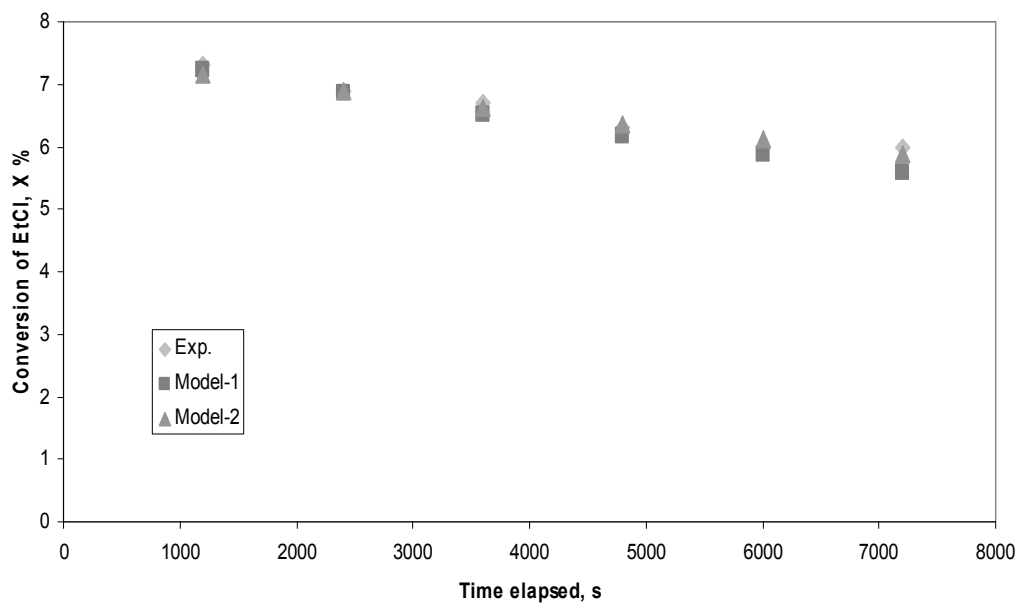


Figure (8); Comparison of the experimental ethyl chloride conversion with the two models, $W_t = 120$ gm, $U = 2.6$ cm/s, $d_p = 75$ micrometer

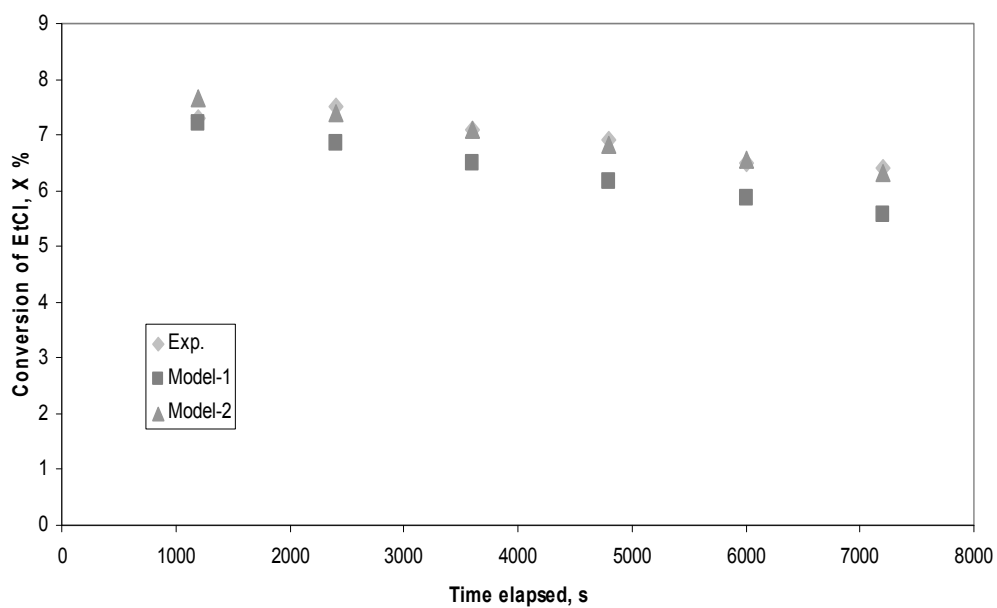


Figure (9); Comparison of the experimental ethyl chloride conversion with the two models, $W_t = 120$ gm, $U = 1.6$ cm/s, $dp = 130$ micrometer

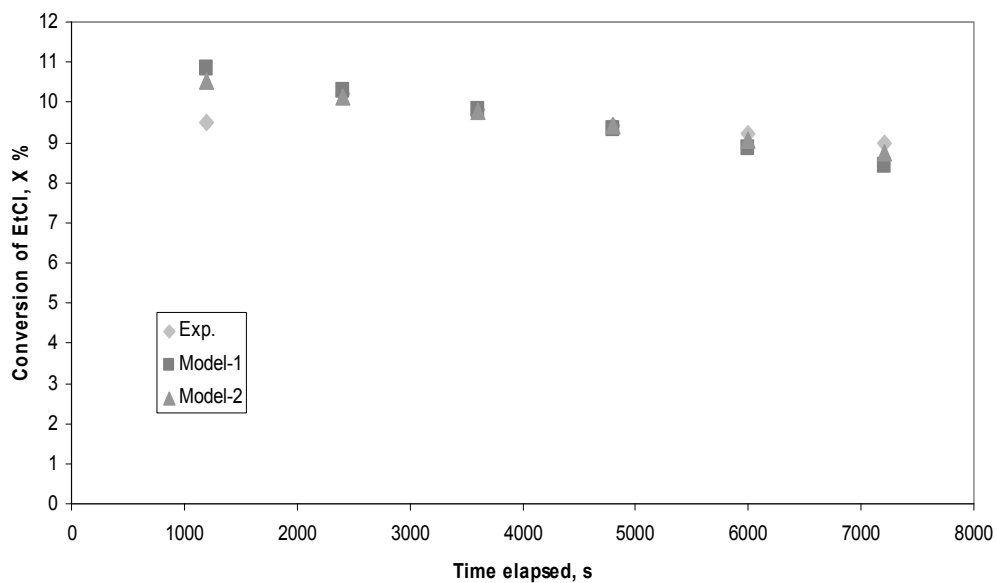


Figure (10); Comparison of the experimental ethyl chloride conversion with the two models, $W_t = 150$ gm, $U = 2.1$ cm/s, $dp = 50$ micrometer

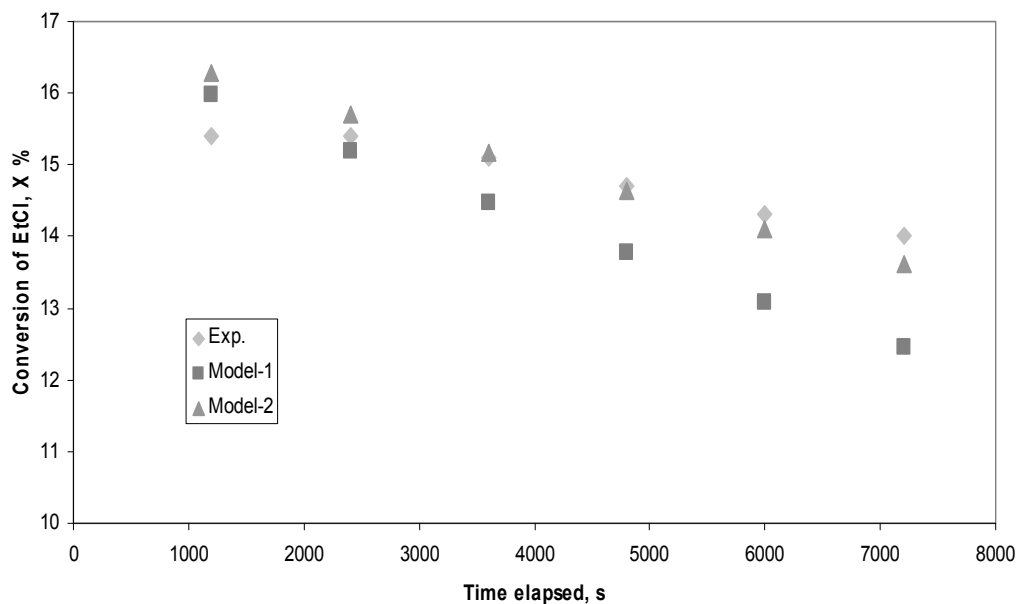


Figure (11); Comparison of the experimental ethyl chloride conversion with the two models, $W_t = 150$ gm, $U = 1.4$ cm/s, $dp = 100$ micrometer

The percentage of Et_2SiCl_2 in the product mixture are predicted and compared with different particle diameters, height of bed, and velocity of the reacted gas, as shown in figures (12), (13), and (14). Figure (12), shows the Et_2SiCl_2 % in the product mixture for different velocities, weight of the constant mass and particle diameter, the overall formation of Et_2SiCl_2 increases with decrease in the reacted gas velocity. These are expected results as the conversion of the EtCl is increasing with decreasing reacted gas velocity. However the percentage of Et_2SiCl_2 with time varies based on weight of contact mass as shown in Figure (13). Higher contact mass weight results in higher percentage of Et_2SiCl_2 . Despite the higher conversion of EtCl at higher particle diameter as shown in figure (6), the percentage of Et_2SiCl_2 show different trend. The percent of Et_2SiCl_2 increase with the decrease in the particle diameter, the data suggest that the selectivity for the desired product increase with smaller particle diameter of Si.

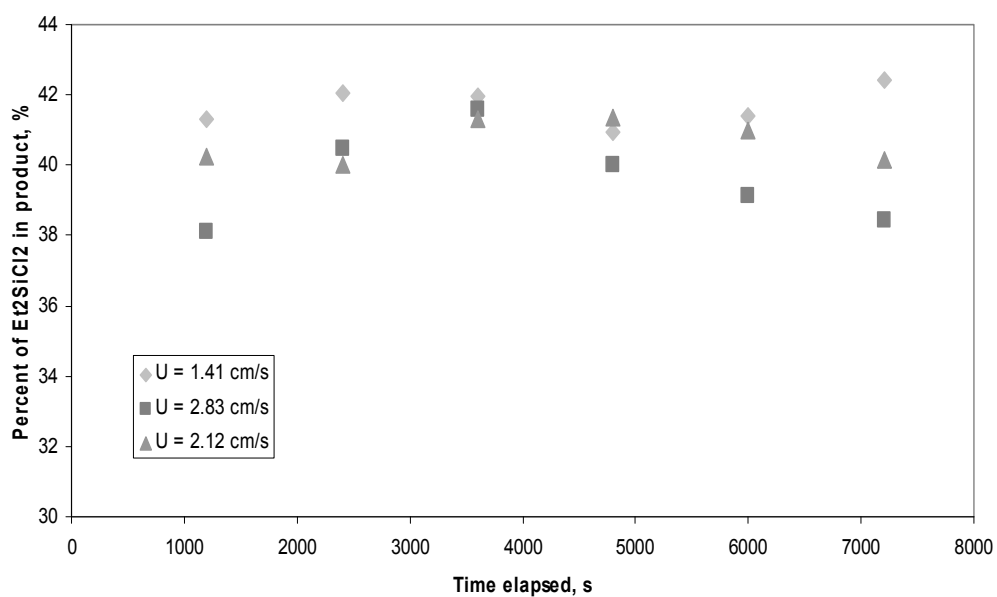


Figure (12); Percent of diethyldichlorosilane in the product at different reactant ethylchloride inlet velocity, $W_t = 150 \text{ gm}$, $d_p = 100 \text{ micrometer}$

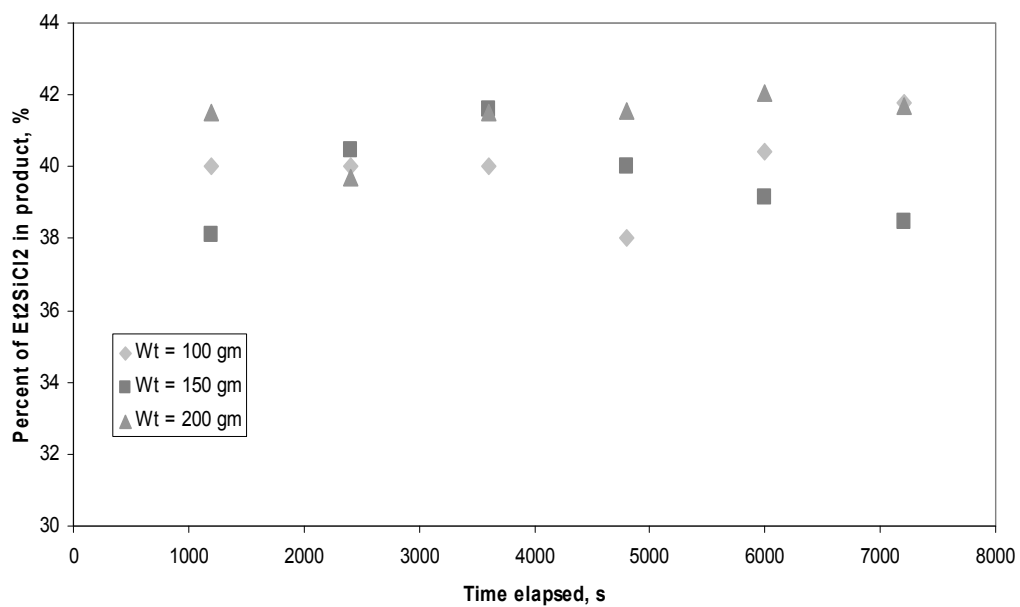


Figure (13); Percent of diethyldichlorosilane in the product at different weight of reactant solid, $U = 2.1 \text{ cm/s}$, $d_p = 100 \text{ micrometer}$

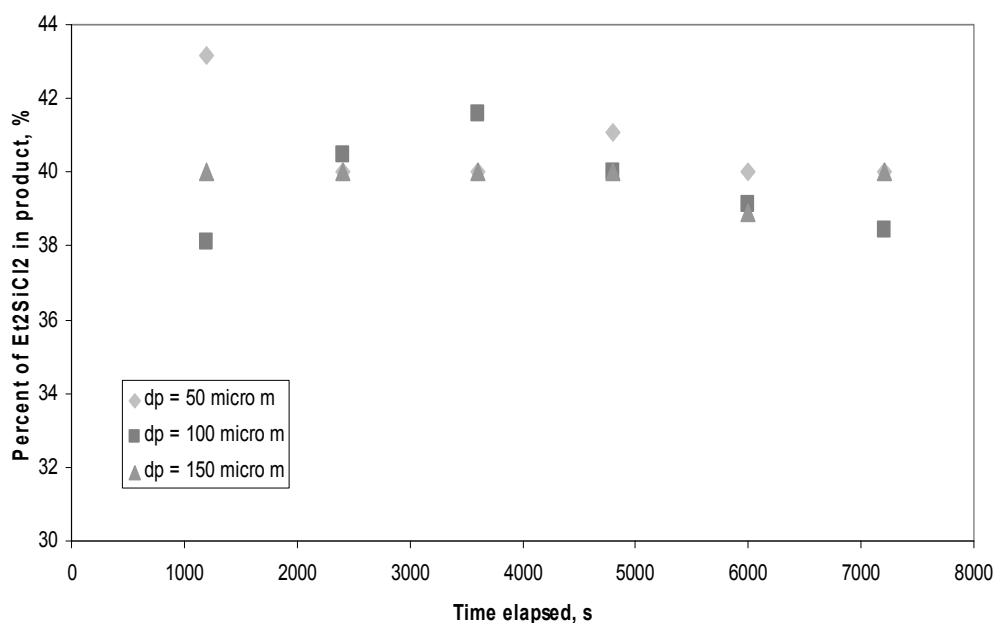
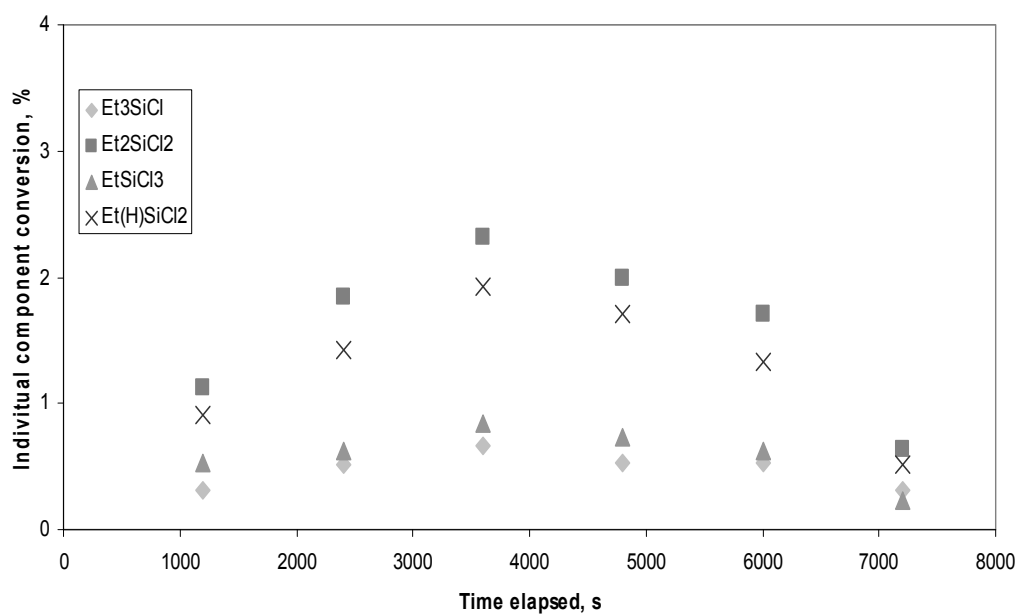


Figure (14); Percent of diethyldichlorosilane in the product at different weight of reactant solid, $W_t = 150$ gm, $U = 2.1$ cm/s

Figures (15), (16), and (17) are plotted to show the percentage of each component in the product at reaction temperatures 200, 250, and 300 C. The three figures show the percentage of desired product Et_2SiCl_2 is the highest of all ethylchlorosilane components for the three temperatures. These results show clearly that the yield of the desired Et_2SiCl_2 product is independent of the variables that have been studied in this paper. CuCl catalyst loading has been kept constant with 15 % of the contact mass for all experiments reported in this paper.



Figure(15); Individual components conversion in the product at 200 C temperatures

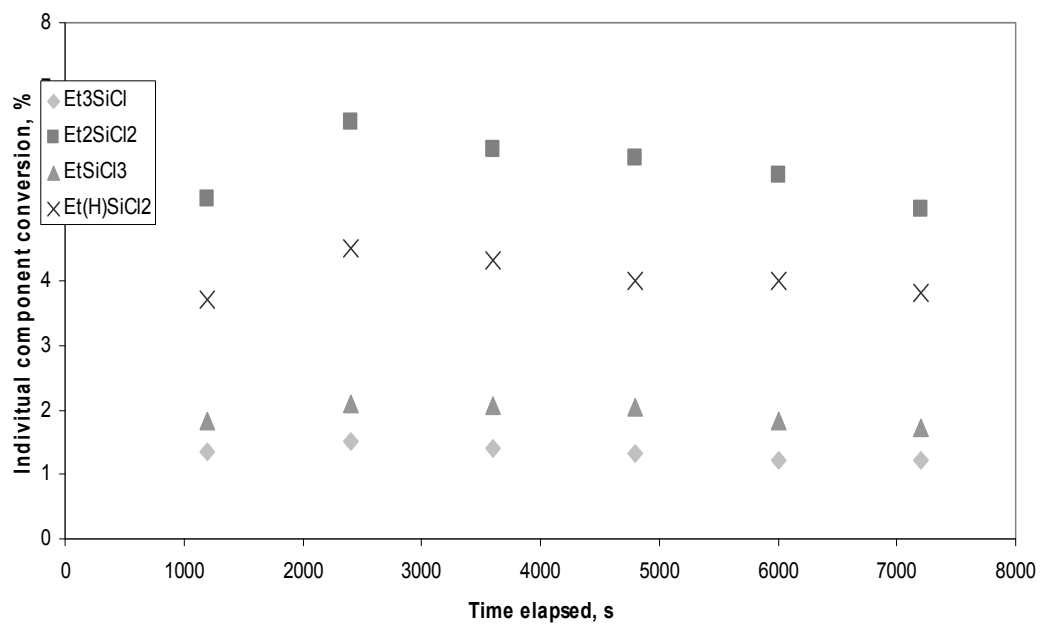


Figure (16); Individual components conversion in the product at 250 C temperatures

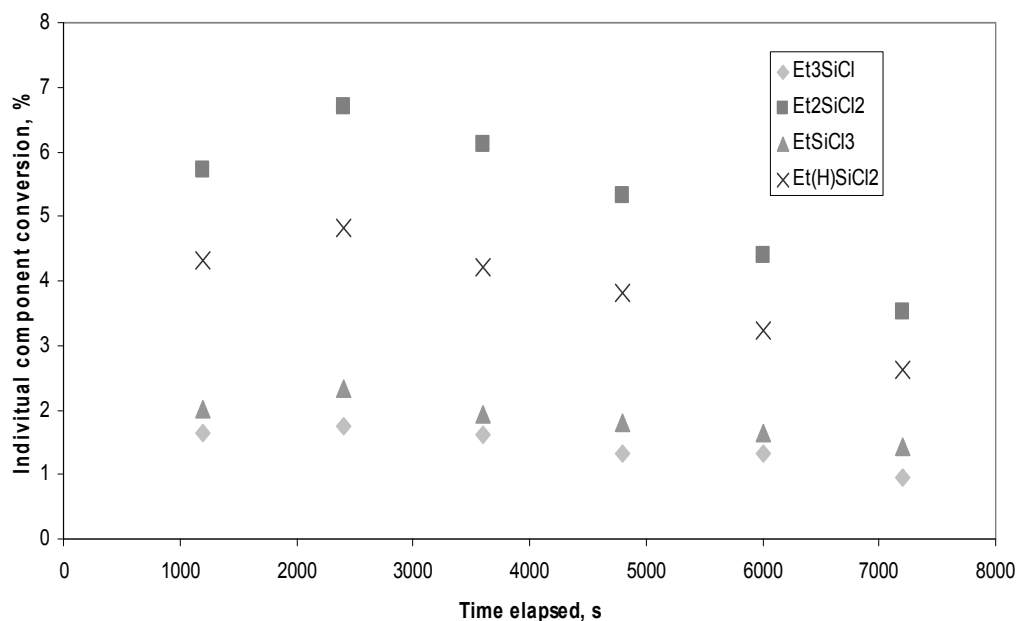


Figure (17); Individual components conversion in the product at 300 C temperatures

Conclusions

The best temperature for reaction of EtCl with Si-CuCl mixtures was 250 C, the temperature reported in literature is between 250-280°C. The highest formation of Et₂SiCl₂ (16%) has been predicted in this experimental work as 250 C. The conversion of EtCl and percentage of Et₂SiCl₂ increased with decreasing the velocity of reacted gas and increasing the weight of the contact mass. Increase in silicon particle diameter shows a low increase in the conversion of EtCl. These results are for the experimental variable ranges used in the experiments; because high decreasing gas velocity may lead to pyrolysis of the product, increasing the weight of the contact mass may leads to slugging which decreases the conversion and finally increasing the particle diameter need higher velocity to fluidize which decreases the conversion. The data predicted from the selected Kinetic and Fluidized bed models show good agreement with the experimental results. The maximum error between experimental results and model prediction was below 9%. The percent of Et₂SiCl₂ in product mixture spread between (36-46%) slightly depends on the variable used.

Nomenclature

Symbol	Definition	Units
a	Deactivation rate	(kgmol/kg.s)
a_b	Interfacial area of bubble based on unit volume	(m ² /m ³)
C_A	Reactant concentration	(kgmol/m ³)
C_{Ao}	Reactant concentration at the inlet to the reactor	(kgmol/m ³)
d_p	Particle diameter	(m)
F_{Ao}	Molar flow rate	(kgmol/s)
H_{mf}	Bed high at minimum fluidization velocity	(m)
K_d	Deactivation rate constant	(1/s)
M, W_t	Weight of bed	(kg)
M_{wt}	Molecular weight	(kg/kgmol)
P_t	Total pressure	(mbar)
Q	Volumetric flow rate	(m ³ /s)
R, R_g	Universal gas constant	(m ³ .atm/kgmol.k)
r_A	Reaction rate	(kgmol/kg.s)
T	Bed temperature	(°C)
T_o	Initial bed temperature	(°C)
U_{mf}	Minimum fluidization velocity	(m/s)
U_o, U	Superficial gas velocity	(m/s)
W_t, M_s	Weight of contact mass	(---)
X, X_A	Fluid (gas) conversion	(---)
ϵ	Voidage of the bed	(---)
ϵ_b	Fraction of bed occupied by bubble	(---)
ϵ_{mf}	Porosity at minimum fluidization	(---)
β	Ratio of gas flow via bubble phase to total gas flow	(---)
ρ_B, ρ_b	Bed density	(kg/m ³)
ρ_g, ρ_f	Gas density	(kg/m ³)
ρ_p	Particle density	(kg/m ³)
$DMDCS, D_i$	Dimethyldichlorosilane	
$Eqs.$	Equations	
$EtCl$	Ethyl Chloride	
$Exp.$	Experimental	
FBR	Fluidized bed reactor	
$Figs.$	Figures	
$MeCl$	Methyl chloride	
$Temp.$	Temperature	
$Theo.$	Theoretical	
GC	Gas chromatography	
r	Correlation coefficient	

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